

PATENT SPECIFICATION

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(54) DEBONDABLE CYANOACRYLATE ADHESIVE COMPOSITION

(71) We, LOCTITE CORPORATION a corporation organised under the laws of the State of Connecticut, United States of America of 705 North Mountain Road, Newington, Connecticut 06111, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to α -cyanoacrylate adhesive compositions, more specifically, to such compositions formulated so as to produce bonds which are relatively weak and can be debonded relatively easily.

Adhesive compositions based upon esters of α -cyanoacrylic acid are well known in the art and have found extensive use, because of their rapid cure speed and excellent long-term bond strength, to a wide variety of surfaces. For instance, tensile shear strength of a steel-to-steel bond typically is greater than 2,200 psi for ethyl cyanoacrylate, and significantly higher in pure tensile strength.

Cyanoacrylate adhesive bonds also tend to be relatively brittle; therefore, the adhesive compositions are often plasticised. Typical plasticisers include the various alkyl esters and diesters and alkyl and aromatic phosphates and phosphonates of U.S. Patent 2,784,127; the diallyl phthalates of U.S. Patent 3,354,128; and the aryl and diaryl ethers of U.S. Patent 3,699,127. These references indicate that, in general, plasticiser concentrations of more than 20 percent by weight of the adhesive composition should be avoided since at higher concentrations, the bond strength would be significantly reduced.

Cyanoacrylate monomer is believed to polymerise primarily by an anionic mechanism. To control premature polymerisation, therefore, ionic inhibitors are

customarily used. These inhibitors are most commonly strong acids, e.g., acidic gases such as nitrogen oxide and sulphur dioxide, at a level of 0.001 to 0.06 percent by weight (see, e.g., U.S. Patent 2,794,788). Other known strongly acidic inhibitors are soluble organic acids, e.g., aryl sulphonic acids, which are typically used at a level of 0.001 to 0.06 percent by weight. While the use of strong acids such as those just mentioned, is important in obtaining good shelf life for the cyanoacrylate monomer, the disadvantage inherent in their use is that they tend to retard the rate of polymerisation, thereby interfering with the effectiveness of the adhesive.

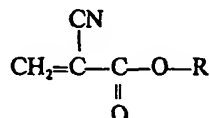
Obviously, the prior art has been directed to maximizing bond strength and shelf life. While rapid reaction rate and good storage stability are always important in a commercial product, it has not heretofore been recognised that a high level of bond strength may not always be desirable. Thus, it would be quite beneficial to have an adhesive formulation which combines the rapid bonding associated with cyanoacrylates with reduced and controlled bond strength, along with the ability to be readily debonded, when desired.

According to the present invention, such an advantageous adhesive composition is provided. The present invention provides a cyanoacrylate adhesive composition having controlled bond strength and adapted for debonding, comprising in admixture at least one polymerisable ester of an α -cyanoacrylic acid, from 20 percent to 60 percent by weight of the composition of a plasticiser which is miscible with the ester, and from 0.015 percent to 0.15 percent by weight of the composition of a carboxylic acid which is soluble in the ester.

The invention also relates to a method for preparing the above adhesive composition by mixing the component ingredients or dissolving the plasticiser and the carboxylic

acid in the cyanoacrylate. The invention further relates to the use of such adhesive composition for bonding objects and subsequently debonding them by applying the composition to a surface of one of the objects, placing that surface in abutting relationship with a mating surface until the adhesive has cured, and then subjecting the bond to heat or solvent action to effect debonding.

The monomeric α -cyanoacrylate esters of this invention are those well known to the art and generally conform to the formula:



wherein R is a C_1 to C_{16} alkyl, alkenyl, cyclohexyl, phenyl, haloalkyl, arylalkyl or acylalkyl group, and mixtures thereof. Preferably, a single ester will be used and R will be a C_1 to C_8 alkyl, alkenyl or cyclohexyl group, most preferably, methyl or ethyl.

The above monomers are generally prepared by the condensation of an ester of cyanoacetic acid with formaldehyde followed by thermal depolymerisation and fractional distillation under vacuum to separate the monomer. Appropriate procedures are described in, for example, U.S. Patents Nos. 2,467,926; 2,467,927; 2,721,858; 2,763,677; 2,784,215; 3,254,111; 3,577,394; and 3,639,361, and other references.

The second required ingredient in the adhesive composition is a plasticiser. The key property of the plasticiser is that it be fully miscible, and compatible; within the concentration range noted below, with the cyanoacrylate. By the term "compatible" is meant that the material does not cause gellation or settling of the mixture. The function of the plasticiser is to weaken the ultimate bond strength of the cured adhesive; therefore, the plasticiser is to be used in relatively high concentration, namely from 20 percent to 60 percent by weight of the total adhesive composition. Preferably, the plasticiser content will be 30 percent to 40 percent by weight. A considerable variety of plasticisers are suitable for use in this invention and their selection according to the criteria above stated will be a matter of straightforward experimentation in any given case. The preferred plasticisers fall into various broad classes, as follows:

(a) aryl and diaryl ethers, such as diphenyl ether and its halogen-substituted derivatives; each aryl ring with its

substituents, if any, may contain up to 20 carbon atoms;

(b) alkyl and alkenyl esters of acids of the fumaric acid series, such as dialkyl fumarate and diallyl maleate; each alcoholic portion may contain up to 12 carbon atoms, but preferably 4 to 8 carbon atoms;

(c) alkyl and alkenyl esters of acids of the oxalic acid series, such as diallyl oxalate, dioctyl azelate, and diallyl sebacate the number of carbon atoms in the alcoholic portion will preferably be as in (b), above;

(d) alkyl and alkenyl esters of acids of the phthalic acid series, whether ortho, meta or para, such as diallyl phthalate, dibutyl phthalate, isobutyl phthalate, and ethyl hexyl phthalate; again the number of carbon atoms in the alcoholic portion will preferably be as in (b), above;

(e) alkyl and alkenyl esters of various other unsaturated dicarboxylic acids, such as diallyl itaconate.

Of the above plasticisers, those of groups (a), (c) and (d) are especially preferred. Mixtures of the above plasticisers can also be used. It will be understood that the above list of plasticisers is not intended to be limiting. Other plasticisers can be used, provided that they meet the miscibility and compatibility criteria described above.

The third required ingredient in the adhesive composition is a carboxylic acid or polycarboxylic acid. The key property of the acid is that it be soluble, within the concentration range noted below, in the cyanoacrylate. The acid should be relatively weak, that is, its pK_a should not be below 1.0 and preferably should be in the range of 1.3 to 6.0. The precise function of the carboxylic acid is not well understood; however, without intending to be bound to any particular theory, it is believed that the acid tends to limit polymer chain length. However, the acid may also provide surface effects which tend to enhance adhesion and thereby regulate the weakening effect of the plasticiser. The most desirable acids are those which, in addition to being soluble, do not substantially contribute to degradation of bond strength during storage of bonded parts over periods of days or weeks, or substantially increase fixture or cure time. The acid also appears to aid in disassembly of the bond, for example, by application of solvent, where desired.

The concentration of the carboxylic acid may vary from 0.015 percent to 0.15 percent by weight of the adhesive composition. The acid concentration chosen for any given situation will depend on the particular properties of the acid in relation to the

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above criteria. The preferred concentration, however, will usually be in the range of 0.025 percent to 0.075 percent by weight. It will also be appreciated that since the acid and the plasticiser have a certain degree of individual ability to control bond strength, a considerable range of adhesive properties can be obtained by varying the proportions of these ingredients, as will be found by straightforward experimentation.

The preferred soluble organic acids fall into the following categories:

(a) alkyl and alkenyl monocarboxylic acids and their halo and cyano derivatives, such as mono- and dichloroacetic acid, cyanoacetic acid, and oleic acid; the alkyl or alkenyl moiety preferably will have from 1 to 25 carbon atoms, more preferably from 1 to 17 carbon atoms;

(b) aromatic monocarboxylic acids, such as benzoic acid and phenyl acetic acid, and the halo and lower alkyl and alkenyl derivatives (e.g., from 1 to 4 carbon atoms) of such acids, for example, toluic acid and chlorobenzoic acid;

(c) aliphatic dicarboxylic acids of the oxalic acid series, such as oxalic acid and malonic acid, wherein the aliphatic portion may be substituted with halo and lower alkyl and alkenyl groups (e.g., from 1 to 4 carbon atoms).

A variety of additional materials may also be present in the adhesive composition. As has been mentioned, the cyanoacrylate monomer will usually contain an inhibitor of anionic polymerisation, such as an acidic gas. More recently, sultone stabilisers have been developed (see U.S. Patent 3,742,018). It is also usually desirable to include an inhibitor of free radical polymerisation, such as compounds of the phenolic type, for example, hydroquinone, its monomethyl ether or *p*-tert.-butyl catechol. In some applications it may be advantageous to include dyes and viscosity modifiers as well. These materials, as well as the concentrations of their use, are known in the art and form no part of the present invention. A worthwhile summary of known formulations may be seen in U.S. Patent 3,699,127.

As has been indicated, a particular advantage of the adhesive compositions of this invention is that their bonds can be destroyed relatively easily, thereby permitting disassembly of bonded parts. This property is highly desirable in applications where, for instance, rapid fixturing but weak ultimate strength is desired or where a small object to be adhered to a jig or fixture for machining but is subsequently to be detached from the jig or fixture. The compositions of this invention are uniquely

adapted to such needs since they quickly (e.g., within one hour or less) form a secure bond having tensile strength of 1,000 psi or more, but yet the parts can be very rapidly debonded, typically within 10 minutes or less. This combination of properties greatly improves efficiency in certain manufacturing operations. Debonding can be readily accomplished thermally, such as by heating the bond line to 200 to 300°F by oven or induction heat. A variety of solvents, such as nitromethane, acetone, acetonitrile or dimethylformamide, will also dissolve the bond. A particularly desirable feature of the present compositions is that the adhered parts may also be debonded by an aqueous surfactant solution containing, e.g., 1 to 5 percent by weight of the surfactant. A wide variety of water-soluble surfactants may be employed, but a preferred surfactant is a potassium aryl alkyl sulphonate sold under the trade name "Ninate 415" manufactured by Stepan Chemicals, Inc., Northfield, Illinois, U.S.A.

Mild heating (e.g., about 50°C) of the solution is helpful. The presence of the carboxylic acid has been found to be beneficial in this context. While the mechanism is not understood, it appears that it reduces the water resistance of the bond. Whether a solvent or aqueous bath is used, the bath should be agitated. An especially effective form of agitation is provided by an ultrasonic transducer.

The following examples illustrate the invention but are not intended to be limiting in any way.

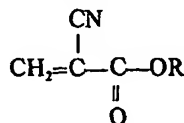
EXAMPLE I.

An adhesive composition solution was prepared as follows. 2.5 grams of a phenolic free radical inhibitor and 0.25 gram of oxalic acid were dried for about 2 hours at 60°C and 4 mmHg pressure. These dried ingredients were weighed into a clean, dry polyethylene container. Then 175.0 grams of dibutyl phthalate and 322.25 grams of ethyl cyanoacrylate monomer were weighed into the container. Shaking accelerated the dissolving of the solids. This composition is referred to as "A".

The same procedure was followed using dried cyanoacetic acid instead of oxalic acid and diphenyl ether instead of dibutyl phthalate. This composition is referred to as "B".

A third composition, referred to as "C", was prepared using the same procedure except that 0.37 gram dried benzoic acid was substituted for the oxalic acid.

Typical strength properties for these adhesive formulations are reported in Table I below for the room temperature cure times shown. The tensile lap shear test was performed according to ASTM A109. This



wherein R is a C₁ to C₁₆ alkyl, alkenyl, cyclohexyl or phenyl group.

3. A composition as claimed in Claim 1 or 2, wherein the plasticiser is an aryl or diaryl ether.
4. A composition as claimed in Claim 1 or 2 wherein the plasticiser is an alkyl or alkenyl ester of an acid of the fumaric acid series.
5. A composition as claimed in Claim 1 or 2 wherein the plasticiser is an alkyl or alkenyl ester of an acid of the oxalic acid series.
6. A composition as claimed in Claim 1 or 2 wherein the plasticiser is an alkyl or alkenyl ester of an acid of the phthalic acid series.
7. A composition as claimed in any of Claims 1 to 6 wherein the carboxylic acid is an alkyl or alkenyl monocarboxylic acid or derivative thereof.
8. A composition as claimed in any of Claims 1 to 6 wherein the carboxylic acid is an aromatic monocarboxylic acid.
9. A composition as claimed in any of Claims 1 to 6, wherein the carboxylic acid is an aliphatic dicarboxylic acid of the oxalic acid series.
10. A composition as claimed in any of Claims 1 to 9 which additionally contains an inhibitor of anionic polymerisation.

11. A composition as claimed in any of Claims 1 to 10 which additionally contains an inhibitor of free radical polymerisation. 35

12. A cyanoacrylate adhesive composition having controlled bond strength and adapted for debonding substantially as described with particular reference to any of the Examples. 40

13. A method of preparing a cyanoacrylate adhesive composition as claimed in any of Claims 1 to 12 which comprises dissolving the plasticiser and the carboxylic acid in the polymerisable ester of an α -cyanoacrylic acid. 45

14. A cyanoacrylate adhesive composition when prepared by a method as claimed in Claim 13.

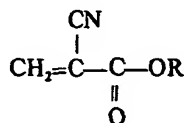
15. A method of debondably adhering and subsequently debonding objects, comprising: 50

I. applying to a mating surface of one of the objects a cyanoacrylate adhesive composition as claimed in any of Claims 1 to 12 or 14; 55

II. placing mating surfaces of the said objects in abutting relationship until the adhesive composition has cured; and

III. debonding the objects by subjecting the bond to heat or solvent action. 60

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9. A composition as claimed in any of Claims 1 to 6, wherein the carboxylic acid is an aliphatic dicarboxylic acid of the oxalic acid series.
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14. A cyanoacrylate adhesive composition when prepared by a method as claimed in Claim 13.

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